

**PATTERN FORMING METHOD**

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**Priority number(s):** JP19940001807 19940113; JP19930004953 19930114

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**Abstract of JP7181687**

**PURPOSE:** To stably form a pattern having high resolution and excellent in dry etching resistance.

**CONSTITUTION:** A photosensitive layer contg. an arom. compd. is formed on a substrate and a photochemical reaction is allowed to take place in the photosensitive layer by patternwise exposing the layer with light having wavelength shorter than the max. wavelength of the 3rd absorption band of the absorption spectrum of the arom. compd. from the long wavelength side and longer than the max. wavelength of the 4th absorption band. The photosensitive layer is then heat-treated if necessary and it is developed to selectively remove or leave the exposed part of the photosensitive layer.

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CLAIMS

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[Claim(s)]

[Claim 1] the process which forms the photosensitive layer containing an aromatic compound on a substrate, and a long wave [ in /, to said photosensitive layer / the absorption spectrum of said aromatic compound ] -- the pattern-formation approach of providing the process which it is [ process ] shorter than the maximum wave length of the 3rd absorption band from a merit side, and pattern exposure of the light of long wave length is carried out [ process ] from the maximum wave length of the 4th absorption band, and produces photochemical reaction in this photosensitive layer, and the process which carries out the development of the photosensitive layer after exposure.

[Claim 2] The pattern formation approach of providing the process which forms on a substrate the photosensitive layer containing the aromatic compound which contains in structure the ring which has the double bond which 4-12 conjugated, the process which pattern exposure of the ultraviolet rays with a wavelength of 180-220nm is carried out [ process ] at said photosensitive layer, and produces photochemical reaction in this photosensitive layer, and the process which carries out the development of the photosensitive layer after exposure.

[Claim 3] The pattern formation approach of providing the process which forms on a substrate the photosensitive layer containing the compound which generates fluorescence at the time of an aromatic compound and exposure, the process which pattern exposure of said photosensitive layer is carried out [ process ], generates fluorescence, and produces photochemical reaction according to an operation of incident light and fluorescence in this photosensitive layer, and the process which carries out the development of the photosensitive layer after exposure.

[Claim 4] The process to which the laminating of the photosensitive layer which contains an aromatic compound on a substrate, and the fluorescence generating layer containing the compound which generates fluorescence at the time of exposure is carried out, The pattern formation approach of providing the process which pattern exposure of said photosensitive layer and the fluorescence generating layer is carried out [ process ], generates fluorescence in this fluorescence generating layer, and produces photochemical reaction according to an operation of incident light and fluorescence in this photosensitive layer, and the process which carries out the development of the photosensitive layer and fluorescence generating layer after exposure.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the pattern formation approach used for micro processing in the manufacture process of electronic parts, such as a semiconductor integrated circuit.

[0002]

[Description of the Prior Art] In the field of the electronic parts which need various kinds of micro processing including a semiconductor integrated circuit, the ultra-fine processing technology containing photolithography is adopted. The following specifically dispels this technique and the pattern formation process is carried out.

[0003] That is, the resist film is first formed on semi-conductor substrates, such as a silicon wafer, with a spin coat method etc. Next, after carrying out pattern exposure of this resist film and producing a photochemical reaction, a development, rinse processing, etc. are performed and a desired resist pattern is formed.

[0004] A detailed line and detailed opening are formed by etching the substrate part to expose by using as an etching-proof mask the resist pattern furthermore obtained. In order to attain high integration of electronic parts in recent years, in said pattern formation process, it is required that the detailed resist pattern of submicron order should be formed. Single wavelength-ization of the exposure light source is performed as the one measure. For example, the pattern formation process which adopted the 5 time higher-harmonic light (wavelength of 213nm) of ArF excimer laser light (wavelength of 193nm), KrF excimer laser light (wavelength of 248nm), or an YAG laser as the light source is developed.

[0005] On the other hand, in said pattern formation process, forming the resist pattern excellent in dry etching resistance is called for in order to perform micro processing more effectively. It is known that it is effective to use current and the compound which has a ring as a resist ingredient, i.e., the photosensitive constituent containing an aromatic compound, about the starting point, and to form the resist film. The photosensitive constituent containing the novolak resin of alkali fusibility used, for example in the mass-production process current [ LSI ] as such a resist ingredient and the quinone diazide which is a sensitization agent, and the photosensitive constituent containing the alkali fusibility resin which has the chemistry magnification mold resist indicated by JP,63-27829,A, i.e., an aromatic series ring, a dissolution retardant, and a photo-oxide generating agent are mentioned.

[0006]

[Problem(s) to be Solved by the Invention] In the conventional pattern formation process, as mentioned above, the exposure light source of short wavelength is adopted, and to form the resist pattern of high resolution is tried. To, adopt the photosensitive constituent which contains an aromatic compound as a resist ingredient on the other hand, and to form the resist pattern excellent in dry etching resistance is tried.

[0007] However, the photosensitive constituent containing said resist ingredient, i.e., the aromatic compound known conventionally, originates in the electron of a ring being excited, and its light absorption especially in a short wavelength field (about 190nm) is very strong. For this reason, if the resist film is formed using the resist ingredient concerned in the pattern formation process which performs exposure which adopted the exposure light source of short wavelength which was mentioned

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above, the resist film may show too strong light absorption at the time of exposure, and photochemical reaction will not fully advance in the resist film as a result.

[0008] It explains in more detail about this point. It is known that the aromatic compound contained in said resist ingredient has three absorption bands which usually originated in the structure of an aromatic series ring. Since the electronic excitation which cannot arise from the symmetric property of an original molecule produced the 1st and the 2nd absorption band from the long wavelength side by molecular vibration, it is not discovered, and it is not [ among these ] so strong. On the other hand, the 3rd absorption band is very mighty.

[0009] In the pattern formation process, when exposure was performed by making into the exposure light source the ultraviolet rays which have the wavelength by the side of long wavelength further from the long wavelength side of said aromatic compound from the wavelength 2nd the 1st and near an absorption band, or these absorption bands, strong light absorption was not seen in said resist film.

[0010] However, when the exposure light source by the radiation of short wavelength etc. is adopted, by said resist film, there is a possibility that it may originate in the 3rd absorption band of said aromatic compound, and strong light absorption may arise. In fact, when the exposure light sources, such as ArF excimer laser light, are adopted to said resist film, photochemical reaction does not fully advance [ light transmittance ] over the whole resist film remarkably low. Consequently, the resist pattern of desired resolution is not obtained.

[0011] If it is in the conventional pattern formation approach as stated above, the resist pattern which shows high resolution when the exposure light source of short wavelength is adopted, and has the outstanding dry etching resistance cannot be obtained, but it has been a problem.

[0012] This invention was accomplished in view of the above-mentioned trouble, and when application to the photolithography in manufacture processes, such as a semiconductor device, is possible and the exposure light source of short wavelength is adopted, it aims at offering the pattern formation approach and the photosensitive constituent which are stabilized and can form the resist pattern excellent in high resolution and dry etching resistance.

[0013]

[Means for Solving the Problem and its Function] The above-mentioned purpose of this invention is attained by the first thru/or fourth pattern formation approach explained below. The process at which the first pattern formation approach of this invention forms the photosensitive layer containing an aromatic compound on a substrate, In said photosensitive layer, are shorter than the maximum wave length of a long wavelength side to the 3rd absorption band in the absorption spectrum of said aromatic compound. And pattern exposure of the light of long wave length is carried out from the maximum wave length of the 4th absorption band, and the process which produces photochemical reaction in this photosensitive layer, and the process which the development of the photosensitive layer after exposure is carried out [ process ], and makes the exposure section of this photosensitive layer remove or remain alternatively are provided.

[0014] Here, "the maximum wave length of an absorption band" means the peak wavelength of the absorption band, i.e., the wavelength of the absorption maximum. Although the absorption band of an aromatic compound is absorption accompanying excitation of the electron in a ring as mentioned above, very feeble 3-fold term electron transition is not included. Moreover, it is thought that two near absorption is the overlapping things strictly from said long wavelength side, and the number of the 3rd absorption band is one in a symmetrical molecule.

[0015] The primary method of this invention is shorter than the maximum wave length of the 3rd absorption band from a specific corresponding to absorption spectrum of aromatic compound concerned to photosensitive layer containing aromatic compound wavelength, i.e., long wavelength, side, and the most characteristic at the point which exposes the light which has long wave length from the maximum wave length of the 4th absorption band. If it puts in another way, it is characteristic at the point of choosing suitably the light which has the specific wavelength according to the presentation of said photosensitive layer, exposing it, and producing photochemical reaction. Since the absorption of light is reduced and permeability improves in a photosensitive layer by adopting such exposure, it continues in

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the whole direction of thickness, and photochemical reaction fully advances. Consequently, it is high resolution and the pattern which originated in the property of the ring in said aromatic compound, and was excellent also in dry etching resistance further can be obtained.

[0016] Hereafter, said primary method is explained to a detail in accordance with a process. First, as the 1st process, on a substrate, after applying the solution (varnish) of the photosensitive constituent which contained the aromatic compound as an indispensable component by for example, the rotation applying method or the dipping method, it dries at 80-130 degrees C preferably, and about 60-150 degrees C (resist film) of photosensitive layers are formed.

[0017] They are III-V, such as a silicon wafer which has the level difference by which various kinds of insulator layers, an electrode, and wiring were formed in the silicon wafer and the front face, for example as said substrate, a blank mask, and GaAs. A compound semiconductor wafer etc. can be mentioned.

[0018] On the other hand, it is the resist ingredient currently generally used and the thing containing at least one sort of aromatic compounds can be used for said photosensitive constituent. The chemistry magnification mold resist which it has a ring in structure as the example, and it has a ring in the resin constituent (positive resist) containing the high molecular compound with which a principal chain may be cut by exposure, and the compound whose solubility improves by exposure, and structure, the resin constituent (negative resist) containing the high molecular compound which can construct a bridge by exposure, and the compound to which solubility gets worse by exposure is mentioned, and a photochemical reaction amplifies by thermal reaction after exposure especially is useful.

[0019] The vinyl system which has rings, such as the benzene ring, a naphthalene ring, and an anthracene ring, in a side chain as an example of said positive resist, or an acrylic compound, Methyl methacrylate, alpha chloro methacrylate, trifluoro ethyl alpha chloro acrylate, A copolymer with acrylic compounds, such as trifluoromethyl acrylate or olefin sulfone, Or the resin constituent containing a photosensitive compound like the polysilane which has a ring like a naphthalene ring in the polymer or side chain of the vinyl system which has rings, such as the benzene ring, a naphthalene ring, and an anthracene ring, in a side chain, or an acrylic compound, The phenol resin containing the naphthoquinonediazide compound which has rings, such as a naphthalene ring, is mentioned.

[0020] The constituent with which the carbon number of the vinyl system which has a ring like the benzene ring, a naphthalene ring, and an anthracene ring in a side chain or an acrylic compound, and an acrylic methacrylate, the methacrylate which has an epoxy group in a side chain or an ester side chain added the photoinitiator cross linking reagent as an example of said negative resist to a copolymer with four or more acrylic compounds, the resin constituent containing a photosensitive compound like the polysiloxane which has rings, such as naphthalene, in a side chain, the phenol resin that has a ring like a naphthol is mentioned.

[0021] In these constituents, sensitizers, such as a bis-azide system compound, may be added if needed. Moreover, the following are illustrated as an example of said chemistry magnification resist.

[0022] The vinyl system which has a ring in a side chain as a chemistry magnification resist of a positive type, or an acrylic compound, Methacrylic-acid tert - Butyl and tert - tert like butoxycarbonyloxy vinyl naphthalene - The compound which has butyl ester in a side chain, tert - The resinous principle which consists of a copolymer with the acrylic which has butyl ester in a side chain, or a vinyl system compound, The compound which may generate an acid by exposure, i.e., a photo-oxide generating agent, and the compound which has at least one association which may be decomposed with an acid if needed, i.e., the resin constituent containing a dissolution retardant, are mentioned. When said dissolution retardant is included in the constituent concerned, said resinous principle is tert. - You may be the copolymer which contains as a component the vinyl system compound which has alkali meltable radicals, such as a methacrylic acid which does not need to have butyl ester and gives alkali solubility.

[0023] As an example of said photo-oxide generating agent, an onium salt like sulfonyl, a sulfonate compound, 4-quinone diazide compound, sulfonium salt, and iodonium salt etc. is mentioned.

Moreover, as an example of said dissolution retardant, it is tert. - A butoxycarbonyl compound, tert - The trimethylsilyl compound protected by the butyl ester compound, the pyranil ether compound, OH,

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or the COOH radical is mentioned. These photo-oxide generating agents and a dissolution retardant may have a naphthalene ring and an anthracene ring in structure according to the loadings.

[0024] In said positive type chemistry magnification resist, the loadings of each component may be set up as the following. Although the loadings of an acid generator change with reinforcement of the generated acid, when it is usually set up in about 0.5 - 30% of the weight of the range and deviates from this range, they have a possibility that the sensibility of a resist may carry out in low, or definition may fall. Moreover, the loadings of a dissolution retardant have a possibility that the sensibility of a resist may fall like the above or definition may fall, also when it is usually set up in about 5 - 99% of the weight of the range and deviates from this range.

[0025] The compound which can construct a bridge in said polymer with the resinous principle which becomes a side chain from the copolymer of the vinyl system which has a ring or an acrylic compound, and an alkali fusibility acrylic, such as an acrylic acid and a vinyl naphthol, or a vinyl system compound as a negative-mold chemistry magnification resist on the other hand, a photo-oxide generating agent, and an acid, i.e., the resin constituent containing a photoinitiator cross linking reagent, is mentioned.

[0026] The triazine and the NAFUCHI lysine compound by which the alkyl halide permutation was carried out besides the compound illustrated in the positive type as an example of said photo-oxide generating agent are mentioned. As the above and a photoinitiator cross linking reagent, the vinyl and the acrylic copolymer which have an epoxy group in a side chain, and a melamine system compound like triazine and a NAFUCHI lysine compound by which the methylol permutation was carried out are mentioned.

[0027] In said negative-mold chemistry magnification resist, the loadings of each component may be set up as the following. Although the loadings of an acid generator change with reinforcement of the generated acid, it is usually set up in about 0.5 - 30% of the weight of the range, and the loadings of a photoinitiator cross linking reagent may be preferably set up in about 0.5 - 40% of the weight of the range. Even when the loadings of which component deviate from the above-mentioned range, there is a possibility that the sensibility of a resist may fall or definition may fall.

[0028] In said photosensitive constituent, the color as the surfactant or acid-resisting agent as a paint film modifier may be added if needed. It can dissolve in a suitable solvent and said photosensitive constituent can prepare the additive of a component which was mentioned above, and others by filtering, respectively. As this solvent, for example Water, a cyclohexanone, an acetone, a methyl ethyl ketone, Ketone solvent, such as methyl isobutyl ketone, methyl cellosolve, methyl-cellosolve acetate, Ethyl Cellosolve, ethylcellosolve acetate, butyl cellosolve, Cellosolve system solvents, such as butyl-cellosolve acetate, ethyl acetate, butyl acetate, Ester solvent, such as isoamyl acetate, ethyl lactate, and methyl lactate, 2-butanol, Alcoholic solvent, such as isoamyl alcohol and a diethylene glycol, Polyhydric-alcohol derivative system solvents, such as ethylene glycol diethylether, diethylene glycol monoethyl ether, and ethyl carbitol, a morpholine, N-methyl -2-pyrrolidone etc. can be mentioned. These solvents may be used independently or may be used in the form of mixture.

[0029] next, the long wave in the absorption spectrum of the aromatic compound contained to said photosensitive layer as the 2nd process following said 1st process -- it is shorter than the maximum wave length of the 3rd absorption band from a merit side, and pattern exposure of the light which has long wave length from the maximum wave length of the 4th absorption band is carried out, and photochemical reaction is produced in a photosensitive layer. Pattern exposure of the ultraviolet rays with which the above-mentioned conditions are filled to said photosensitive layer as concrete actuation is carried out through the mask which has a desired pattern.

[0030] It is important to choose the wavelength of an exposure line suitably at the process concerned according to a convention which was mentioned above according to the structure of the aromatic compound contained in a photosensitive layer, i.e., the structure of a ring included. For example, when a ring is the benzene ring, the ring of exposure wavelength is a naphthalene ring in an about 170-150nm field and the ring of this exposure wavelength is an anthracene ring in an about 210-170nm field, this exposure wavelength can be set up in an about 230-190nm field, respectively. In addition, these wavelength fields change with the substituents introduced into a ring. for example, the thing for which

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what kind of substituent like a halogen radical or a nitro group is introduced into a ring -- a long wave -- about 10nm is shifted to a merit side, and it shifts to a low wavelength side notably in the case where it has a double bond the double bond of a ring and whose conjugation are possible for the substituent concerned.

[0031] Like the above, by choosing exposure wavelength, the light absorption in the exposure section of a photosensitive layer is reduced, and light transmittance can improve remarkably, can cover the whole thickness, and can fully advance photochemical reaction at the process concerned.

[0032] In addition, the photochemical reaction in the exposure section of said photosensitive layer advances according to a device which is based on the class of photosensitive constituent which constitutes a layer, and is different. For example, in the exposure section of the photosensitive layer which consists of said positive resist, the macromolecule chain of a resinous principle cuts, low-molecular-weight-ization advances or an insoluble compound changes with photochemical reaction to the fusibility matter. In the exposure section of the photosensitive layer which consists of said negative resist, the macromolecule chain of a resinous principle constructs a bridge and-dimensional [ 2 ] and the three-dimensions molecular structure are formed.

[0033] Moreover, in the exposure section of the photosensitive layer which consists of said chemistry magnification mold resist, a photo-oxide generating agent generates an acid, this acid disassembles the side chain of a resinous principle, or (in the case of a positive type) a resinous principle constructs a bridge by activation of a photoinitiator cross linking reagent (when it is a negative mold). The acid which heat-treated preferably about 70-160 degrees C of photosensitive layers after pattern exposure at the temperature of 80-150 degrees C especially in this case if needed (postexposure BEKU-EB), and was made to promote a magnification reaction, namely, was generated in the exposure section of a photosensitive layer like the above can be diffused, and the reaction of this acid and other components can be promoted. When the reason for limitation of the temperature in this heat treatment process has a possibility that it may become difficult to make the above-mentioned reaction fully perform that the temperature concerned is less than 70 degrees C and it exceeds 160 degrees C, it is because there is a possibility of the exposure section and the unexposed section of an admiration radiation layer decomposing, or hardening.

[0034] Next, the development of the photosensitive layer after said exposure or heat treatment is carried out, using a predetermined developer as the 3rd process following said 2nd process. Furthermore, a substrate is dried after flushing a developer with pure water.

[0035] At the 3rd process (development) concerned, a photosensitive layer strikes, generally, the exposure section dissolves in a developer alternatively, it is removed, and either the exposure section or the unexposed section and the pattern that is predetermined are formed. In this invention, especially in a last process, since the photochemical reaction of the exposure section is fully advancing, the selectivity of the exposure section and the unexposed section is high, and the pattern of high resolution is formed.

[0036] In addition, the water solution of water or organic alkali like tetramethylammonium hydroxide, and the usual inorganic alkali, an alcoholic solution, etc. can be used for said developer. Moreover, when using the resist from which molecular weight changes with photochemical reactions, organic solvents including ester, such as ketones of a methyl ethyl ketone and methyl isobutyl ketone and butyl acetate, etc. can be used as said developer.

[0037] Next, the second pattern formation approach of this invention is explained. The process at which the second approach of this invention forms on a substrate the photosensitive layer containing the aromatic compound which contains in structure the ring which has the double bond which 4-12 conjugated, In said photosensitive layer, pattern exposure of the ultraviolet rays with a wavelength of about 180-220nm is carried out, and the process which produces photochemical reaction in this photosensitive layer, and the process which the development of the photosensitive layer after exposure is carried out [ process ], and makes the exposure section of this photosensitive layer remove or remain alternatively are provided.

[0038] Here, "the conjugated double bond" means that a double bond is in the condition of having stood in a row every other piece through single bond, and having aligned at the plane. Such a ring has usually

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formed and cyclized six membered-rings.

[0039] The second approach of this invention is characteristic about the component of the photosensitive constituent which exposure and a photosensitive layer constitute namely, use about a solvent, an additive, etc. which formation of a sensitization layer, a development, and each other processings operate and use although it is fundamentally [ as said primary method ] the same. Using the ultraviolet rays of the wavelength (about 180-220nm) limited in detail in order to obtain the pattern of high resolution, the 5 time tidal-wave length (213nm) of an ArF excimer laser (193nm) and an YAG laser is adopted as the light source, and the photosensitive layer containing the compound which has the ring of specific structure corresponding to this is used.

[0040] Generally, an about 180-220nm wavelength field is close to absorption of the ring which has three or less conjugated double bonds, for example, the Ben Seng ring. For this reason, if the photosensitive constituent containing the compound which contains the benzene ring in structure is used in order to raise the etching resistance of a pattern when adopting the ultraviolet rays of the above-mentioned wavelength field and forming a pattern, the light transmittance of a photosensitive layer (resist film) is low, and the photochemical reaction by exposure will cover the whole thickness, and will not fully advance. So, by said second approach, the absorption band is shifted to a short wavelength side using the ring which has four or more conjugated double bonds, and the absorption to the ultraviolet rays of the above-mentioned wavelength field is reduced. Consequently, the light transmittance of the photosensitive layer at the time of exposure can improve, and it can continue in the whole direction of thickness, and photochemical reaction fully advances, it is high resolution and the pattern which originated in the property of said ring and was excellent also in dry etching resistance can be obtained further. Thus, by the second approach, by choosing suitably the structure of the ring of the aromatic compound contained in a photosensitive layer corresponding to the ultraviolet rays of the limited wavelength, duplication in exposure wavelength and the absorption band of the aromatic compound contained in a photosensitive layer is avoided, the light transmittance of a photosensitive layer is raised, and a desired detailed pattern is obtained.

[0041] It is used in the second approach of this invention. The ring concerned is introduced into the molecule frame of the compound which constitutes a photosensitive layer, for example, the principal chain frame of a resinous principle and a side-chain frame, and the frame middle class of other components with the aromatic compound containing the ring which has the double bond which 4-12 conjugated. As an example, it enumerated in said primary method. That by which the ring which has the double bond which 4-12 conjugated was introduced into the frame of the frame of the compound which constitutes a general positive resist, negative resist, and a chemistry magnification mold resist, for example, the principal chain of a resinous principle, a side chain, a photo-oxide generating agent, or a dissolution retardant is mentioned.

[0042] The rings which have said double bond which 4-12 conjugated are the atom of others [ atoms / one or more / which are combined with the ring to frames, such as the benzene ring and a pyridine ring, ], and a ring bonded doubly. A benzene ring frame, a pyridine ring frame, etc. which were permuted as an example by the unit expressed with -R1 =R2- or -R3- (= R4) (1 permutation carbon atom and R4 are [ R1 / R2 ] an oxygen atom, 1 permutation nitrogen atom, or 2 permutation carbon atom for 1 permutation carbon atom, a nitrogen atom, and R3) are mentioned.

[0043] Moreover, said rings may be the benzene ring mentioned above in that it excels in smoothness, a pyridine ring, and a compound ring formed of other monocycles. As an example of the compound ring concerned, a pyrrole, benzofuran, benzothiophene, Indore, benzoxazole, benzothiazole, indazole, a chromene, a quinoline, SHINORIN, phthalazine, quinazoline, a dibenzofuran, a carbazole, an acridine, phenanthridine, a phenanthroline, phenazine, CHIANTOREN, indolizine, a NAFUCHI lysine, a pudding, a pteridine, a fluorene, a benzoquinone, a phthalimide, a phthalic anhydride frame, etc. are mentioned.

[0044] When the ring which has said double bond which 4-12 conjugated is a compound ring which six membered-rings combined, it is desirable at the point whose dry etching resistance of the pattern obtained improves remarkably. As an example of such a compound ring, naphthalene, an anthracene, a

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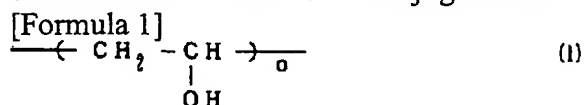
phenanthrene, a pyrene, a naphthacene, a chrysene, 3, 4 benzophenanthrene, perylene, pentacene, and picene are mentioned. Moreover, it is the structure which gives the dry etching resistance which was excellent also in biphenylene or a biphenyl. When the ring concerned is especially chosen from naphthalene, an anthracene, and a phenanthrene, finally the transparency and dry etching resistance of a pattern are raised.

[0045] As for the ring which has 12 or less or more 4 conjugated double bond by said second approach, it is desirable to occupy at least 60 % of the weight or more in all the rings in a photosensitive constituent. This reason is because there is a possibility of checking the light transmission nature of a photosensitive layer, when it exceeds 60 % of the weight. 75 - 100% of the weight of the range is more desirable. Moreover, as for the amount of the above-mentioned specific aromatic compound in the solid content of a photosensitive constituent, it is desirable that it is [ at least 10 % of the weight or more ] less than 90 % of the weight. This reason is because there is a possibility that the dry etching resistance of the pattern obtained as the amount of the aromatic compound concerned is less than 10 % of the weight may fall, and the light transmission nature of a photosensitive layer may fall that it is 90 % of the weight or more conversely. The amount of the more desirable above-mentioned aromatic compound is 20 - 50 % of the weight.

[0046] When said ring is permuted by the protective group of a hydroxyl group or a hydroxyl group like OR' (R' is tert-butyl and tert - butoxycarbonyl radical), finally alkali solubility is given to the compound containing the ring concerned after exposure. Therefore, it is very suitable for the pattern formation process which adopts an alkali development. Moreover, when the above-mentioned aromatic series ring is permuted by a sulfonic acid group, its salt, the amino group, or its salt, since water solubility is given, the compound containing the aromatic series ring concerned is suitable for the pattern formation process which adopts a water development.

[0047] As for the photosensitive constituent (resist) containing the aromatic compound which has a specific ring which was mentioned above, it is desirable that the melting point is 50 degrees C or more, and its thing [ as opposed to water or an organic solvent at the point of spreading nature ] which has high solubility is desirable.

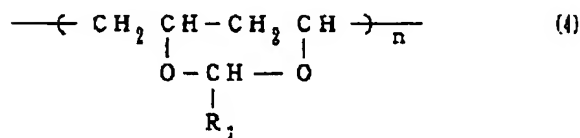
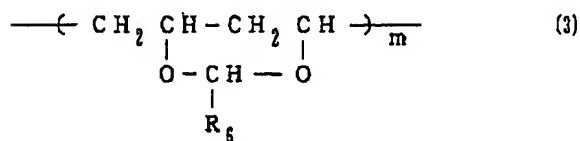
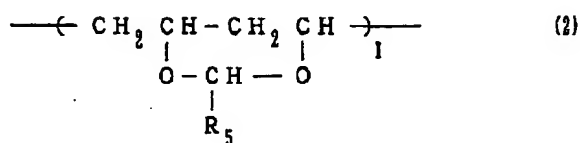
[0048] The photosensitive constituent (A) shown below as a suitable photosensitive constituent as a photosensitive constituent containing the aromatic compound containing the ring which has the double bond which the above 4-12 conjugated is mentioned. A compound (A) is [0049] in a frame.



And following (2) It is the photosensitive constituent which consists of the acetal resin which has a part for a kind of structured division of (3) and (4) at least, an epoxy compound which has a naphthalene ring in a frame, and a compound which generates an acid or alkali by the exposure of light or ionizing radiation.

[0050]

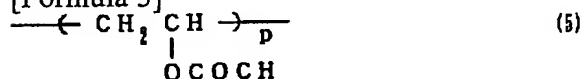
[Formula 2]



(ただし、 $\text{R}_5$  はアルキル基、 $\text{R}_6$  はカルボキシル基  
またはアミノ基を含むアルキル基、 $\text{R}_7$  は芳香環を示し、  
 $1, m, n$  は0を含む正の整数であり、  
かつ  $1 + m + n > 0$ 、0は0以外の正の整数)

[0051] The acetal resin in the above-mentioned photosensitive constituent (A) uses polyvinyl alcohol as a raw material, and is it  $\text{R}_5$  -  $\text{R}_7$  It is obtained by the approach of acetalizing the aldehyde which has a substituent using an acid catalyst. It is [0052] in a frame in addition to above-mentioned (1) - (4) as a residual unreacted part of the polyvinyl acetate which is the raw material of polyvinyl alcohol according to the above-mentioned approach.

[Formula 3]



(ただし  $p$  は正の整数)

Although it \*\*\*\*\* , you may have a part for this structured division (5). The molecular weight of the above-mentioned acetal resin has desirable or more 1000 thing which is 300,000 or less. If it deviates from this range, the solubility to a solvent will be checked remarkably.

[0053] Although the total amount for the structured division of (2) changes in the above-mentioned acetal resin also with solvents in which resin is dissolved, when making it dissolve in water or alcoholic solvent, less than [ 50mol% ] is desirable, and when you make it dissolve in organic solvents other than water or alcoholic solvent, it is desirable that it is more than 50mol% of the whole. If it deviates from these range, the solubility over a solvent will be checked remarkably. Moreover, as for a part for the structured division of (3) in the above-mentioned acetal resin, or (4), it is desirable that it is less than [ 50mol% ]. If it deviates from this range, the crosslinking reaction between resin will arise in a synthetic process, and target resin will no longer be obtained.

[0054] that into which it is introduced by part for the structured division of the above (3) since the amount of [ the solubility over an acid and / of (4) ] structured division promotes the solubility over alkali -- it is -- respectively -- at least -- more than 1mol% -- being introduced is desirable. It is five-mol% - 30-mol% more preferably.

[0055] Moreover, as the compound which generates an acid by the light or ionizing radiation in the above-mentioned photosensitive constituent (A), i.e., a compound which generates an acid by exposure, (photo-oxide generating agent), an onium salt, orthoquinone diazido sulfonate, a sulfonyl compound, sulfonate, an organic halogenide, etc. are mentioned. as said onium salt, the diazonium salt which uses a fluoroboric-acid anion, a hexafluoro antimonate anion, a hexa fluoroarsenic acid anion, a trifluoromethane sulfonate anion, or a PARATORU en sulfonate anion as a counter ion, phosphonium salt, and sulfonium salt mention, for example -- having -- inside -- the onium salt and diaryl sulfide of trifluoro methysulfonic acid and a thoria reel sulfide, and diaryl one -- Io -- since the onium salt with

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DAIDO is highly sensitive, it is suitable. An allyl compound sulfonyl methane derivative as shown in a Japanese-Patent-Application-No. No. 53729 [ four to ] specification as said sulfonyl compound, a JIARIRUJI sulfonyl methane derivative, a diaryl MECHIRUJI sulfonyl methane derivative, a methylsulfonyl methane derivative, a dimethyl sulfonyl methane derivative, its diazotation object, etc. are mentioned, for example, screw (phenyl sulfonyl) methane, a phenyl sulfonyl acetonitrile, 1 methyl 2 (phenyl sulfonyl) (methyl) benzene, etc. are suitable. Said organic halogenide is a compound which forms halide acid, and what was indicated by U.S. Pat. No. 3515552, U.S. Pat. No. 3536489, U.S. Pat. No. 3779778, and the West German patent public presentation official report No. 2243621 is mentioned. Moreover, the compound indicated by JP,54-74728,A, JP,55-24113,A, JP,55-77742,A, JP,60-3626,A, JP,60-138539,A, and JP,50-36209,A is used for other photo-oxide generating agents, and it gets.

[0056] When the above photo-oxide generating agent is illustrated concretely, JI (PARATA challis butylbenzene) diphenyliodonium trifluoromethane sulfonate, Benzoin tosylate, alt.nitrobenzyl PARATORUEN sulfonate, Triphenylsulfonium trickle OROMETANI sulfonate, Tori (tertiary buthylphenyl) sulfonium trifluoromethane sulfonate, BENZENIJAZONIUMUPARA toluenesulfonate, 4 -(G n propylamino)- BENSONIUMU tetrafluoroborate, 4-P-tolyl-mercapto - 2 Five - Diethoxybenzene diazonium hexafluorophosphate, Tetrafluoroborate, diphenylamine -4 - Diazonium sulfate, 1, 8-NAFUTARUIMI dill triflate, a naphthalene content onium salt, (NAT-103, NAT-105, NDS-103, NDS-105 acid generator (the Midori chemistry company make: CAS [131582-00-8], [137867-61-9], and [110098-97-0])), 4-methyl -6 - TORIKURORO methyl -2 - A pyrone, 4-(3, 4, 5-trimethoxy-styryl)-6 - TORIKURORO methyl -2 - Pyrone, 4-(4-methoxy-styryl)-6--(3, 3, and 3-TORIKURORO-propenyl) 2 - Pyrone, 2-TORIKURORO methyl-benzimidazole 2-tribromomethyl-quinolone, 2, 4-DOMECHIRU -1 - TORIPUOMO acetyl-benzene, a 4-dibromo acetyl-benzoic acid, 1, 4-screw-dibromo methyl-benzene, tris-dibromo methyl - S - Triazine, 2-(6-methoxy-naphthyl-2- IRU)-4 and 6- Screw-TORIKURORO methyl - S - Triazine, 2-(naphthyl-1- IRU)-4 and 6- Screw-TORIKURORO methyl-S-triazine, 2-(naphthyl-2- IRU)-4 and 6- Screw-TORIKURORO methyl - S - Triazine, 2-(4-ethoxyethyl-naphthyl-1- IRU)-4 and 6- Screw-TORIKURORO methyl - S - Triazine, 2-(benzoPIRANI-3- IRU)-4 and 6- Screw-TORIKURORO methyl - S - Triazine, 2-(4-methoxy-ANTORASHI-1- IRU)-4 and 6- Screw-TORIKURORO methyl - S - Triazine, 2-(FENANCHI-9- IRU)-4 and 6- Screw-TORIKURORO methyl - S - Triazine, o-naphthoquinonediazide -4 - Sulfonic-acid chloride etc. is mentioned.

[0057] For the loadings to the other solid content of this photo-oxide generating agent, although it cannot generally \*\*\*\*\* depending on the acid generating effectiveness of a photo-oxide generating agent, it is [ the 0.01-20 weight section and ] usually \*\*\*\* better \*\* to consider as the range of the 0.2-10 weight section more preferably. This reason will become insufficient [ that blending effect ], if the loadings of said acid generator are \*\*\*\*\*ed to less than 0.01% of the weight, and when 20 weight sections are exceeded on the other hand, it has a possibility that paint film nature may get worse.

[0058] A carbamate compound and a sulfonamide compound are mentioned as the compound which generates alkali by the above-mentioned light or ionizing radiation, i.e., a compound which generates alkali by exposure, (optical alkali generating agent). Especially, a nitrobenzyl cyclohexyl carbamate, a dimethoxy benzyl cyclohexyl carbamate, N-cyclohexyl-methylphenyl sulfonamide, N-cyclohexyl-naphthyl sulfonamide, etc. may be used suitably. For the loadings to the other solid content of this optical alkali generating agent, although it cannot generally \*\*\*\*\* depending on the generating effectiveness of an optical alkali generating agent, it is [ the 0.1-20 weight section and ] usually \*\*\*\* better \*\* to consider as the range of the 0.5-10 weight section more preferably. This reason is that there is a possibility that paint film nature may get worse when that blending effect will become inadequate if the loadings of said optical alkali generating agent are \*\*\*\*\*ed to less than 0.1% of the weight, and 20 weight sections are exceeded on the other hand.

[0059] When the above-mentioned photosensitive constituent (A) contains the epoxy compound which contains a naphthalene ring in a frame, sensibility rises remarkably. Although all they correspond if the epoxy compound which contains this naphthalene ring in a frame is a naphthalene compound which has two or more epoxy groups in 1 molecule at least more preferably than one or more, the compound and epoxy resin which carried out epoxidation of the polyhydroxy naphthalene compound under base

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existence by epichlorohydrin are used suitably. As this polyhydroxy naphthalene compound, they are the naphthols like dihydroxy naphthalene, the naphthol novolak compound which condensed them with formaldehyde. For the loadings to the other solid content of this epoxy compound, although it cannot generally \*\*\*\*\* depending on the molecular weight of an epoxy compound, it is [ the 1-70 weight section and ] usually \*\*\*\* better \*\* to consider as the range of the 5-50 weight section more preferably. This reason will become insufficient [ that blending effect ], if the loadings of an epoxy compound are \*\*\*\*ed to less than 1% of the weight, and when 70 weight sections are exceeded on the other hand, it has a possibility that thermal resistance, spreading nature, and light transmission nature may get worse.

[0060] A photosensitive constituent (A) constructs a bridge over high sensitivity according to an operation of photo-oxide and a base generating agent, and the acetal resin of specific structure is the photosensitive high constituent of transparency. By the acid and the base, intramolecular branching transfers to intermolecular bridge formation, bridge formation, insolubilization, and film contraction arise, and acetal resin can be used as negative resist. Since you gathered bridge formation effectiveness to the photosensitive constituent based on this acetal resin, and you made it high-sensitivity-ize further to it and that epoxy compound had a naphthalene frame by adding an epoxy compound in it, the carbon content was able to be raised and dry etching resistance was able to be improved. Since the energy of excitation of a double bond makes a naphthalene frame low and can improve the transparency of 180-220nm by conjugate, it can also improve the light transmission nature of 180-220nm wavelength.

[0061] Moreover, the photosensitive constituent (B) containing the compound which generates an acid or alkali by the exposure of the polymer which contains the vinyl compound which has an epoxy group in a side chain as a photosensitive constituent suitable as a photosensitive constituent containing the aromatic compound containing the ring which has the double bond which 4-12 conjugated, the polyhydroxy compound which contains a naphthalene ring in a frame and light, or ionizing radiation is mentioned.

[0062] As a polymer containing the vinyl compound which has the above-mentioned epoxy group in a side chain, the polymer of a polymer [ of a JIRUMETA chestnut rate ], polymer [ of allyl glycidyl ether ], 1, 2-epoxy 5, polymer [ of 9-cyclo dodecane diene ], 1, and 2-epoxy 5-hexene or the polymer of a methylvinyl oxirane is mentioned, for example.

[0063] The dry etching resistance of a photosensitive constituent and alkali solubility can be raised as it is the 3 yuan copolymer of the vinyl compound which has an epoxy group in a side chain especially as a polymer containing the vinyl compound which has the above-mentioned epoxy group in a side chain, the vinyl compound which has an aromatic series ring in a side chain, and the vinyl compound which has a carboxylic acid in a side chain.

[0064] As a vinyl compound which has a ring in a side chain, styrene, BINIFU naphthalene, a vinyl anthracene, vinylcarbazole, a vinyl phenol, vinyl NATTORU, chloro methyl styrene, etc. are mentioned.

[0065] Moreover, as a vinyl compound which has a carboxylic acid in a side chain, an acrylic acid, a methacrylic acid, and a maleic anhydride are mentioned. On the occasion of copolymerization, these acids are protected by the trimethylsilyl radical, tertiary butyl, etc., carry out deprotection later, and if a carboxyl group is produced as a result, they will not be cared about.

[0066] As for the presentation ratio in the above-mentioned 3 yuan copolymer, it is desirable for the vinyl compound with which the vinyl compound with which the vinyl compound which has an epoxy group in a side chain has a 5-40mol% ring in a side chain has 10-60-mol % and a carboxylic acid in a side chain to be in the 10-50-mol range of %. When it deviates from this range, there is a possibility that which property of sensibility, alkali solubility, and the dry etching resistance may fall.

[0067] Moreover, this photosensitive constituent is made to contain the polyhydroxy compound which contains a naphthalene ring in a frame as a cross linking agent. As the above-mentioned polyhydroxy compound, the naphthols like dihydroxy naphthalene, the naphthol novolak compound which condensed them with formaldehyde are mentioned, for example. The loadings in the other solid content of this polyhydroxy naphthalene compound are prescribed by the amount of the epoxy group of other solid content, and it deals in them. Usually, it is [ the one - 50 mol section of an epoxy total amount, and ]

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\*\*\*\* better \*\* to consider as the range of 5 -50-mol section more preferably. This reason will become insufficient [ that blending effect ], if the loadings of a polyhydroxy compound are \*\*\*\*ed to less than 1% of the weight, and when the 50-mol section is exceeded on the other hand, it has a possibility that spreading nature and solubility may get worse.

[0068] The compound which furthermore generates an acid or alkali by the above-mentioned light or ionizing radiation is blended. The same compound as what is used for a photosensitive constituent (A) as a compound which generates an acid or alkali by the light or ionizing radiation used for a photosensitive constituent (B) is mentioned. Moreover, it is the same as that of a photosensitive constituent (A) also about those loadings.

[0069] The vinyl system polymer with which a photosensitive constituent (B) has an epoxy group in a side chain constructs a bridge over high sensitivity by photo-oxide and the alkali generating agent, and is the photosensitive high constituent of transparency. By the acid and the base, bridge formation, insolubilization, and film contraction arise and the vinyl system polymer which uses epoxy as a side chain can be used as negative resist. Since gathered bridge formation effectiveness to the vinyl system polymer which has an epoxy group in a side chain, it was made to attain the dissolution disposition top of high-sensitivity-izing and the unexposed section further and the polyhydroxy compound had a ring by adding a suitable quantity of a polyhydroxy compound in it, dry etching resistance was able to be improved. Since a naphthalene frame is furthermore included in the ring, light transmission nature with a wavelength of 180-220nm can also be improved.

[0070] Said photosensitive constituent (A) and a photosensitive constituent (B) are prepared by dissolving in water or an organic solvent and filtering resin and an additive which were mentioned above. As this organic solvent, ester solvent, such as cellosolve system solvents, such as ketone solvent, such as a cyclohexanone, an acetone, a methyl ethyl ketone, and methyl isobutyl ketone, methyl cellosolve, methyl-cellosolve acetate, ethylcellosolve acetate, and butyl-cellosolve acetate, ethyl acetate, butyl acetate, isoamyl acetate, and gamma-butyl lactone, dimethyl sulfoxide, a dimethylformamide N-methyl pyrrolidone, etc. can be mentioned, for example. These organic solvents may be used independently or may be used in the form of mixture. Moreover, fatty alcohol, such as a xylene, toluene, or isopropanol HIPIRU alcohol, may be in these by optimum dose \*\*\*\*.

[0071] Furthermore, the above-mentioned photosensitive constituent may blend the color as the surface active agent or other polymers, for example, the polymethylmethacrylate, the polymethyl acrylate, the propylene oxide-ethylene oxide copolymer, the polystyrene, or the acid-resisting agent as a paint film modifier other than the component mentioned above if needed.

[0072] Next, the third pattern formation approach of this invention is explained. The process at which the third pattern formation approach of this invention forms on a substrate the photosensitive layer containing the compound which generates fluorescence at the time of an aromatic compound and exposure, Pattern exposure of said photosensitive layer is carried out, fluorescence is generated, and the process which produces photochemical reaction according to an operation of incident light and fluorescence in this photosensitive layer, and the process which the development of the photosensitive layer after exposure is carried out [ process ], and makes the exposure section of this photosensitive layer remove or remain alternatively are provided.

[0073] It is characteristic about the component of the photosensitive constituent which exposure and a photosensitive layer constitute namely, use about a solvent, an additive, etc. which formation of a sensitization layer, present condition processing, and each other processings operate and use also about the third approach of this invention although it is fundamentally [ as said primary method ] the same. In detail, it is characteristic at the point which uses the photosensitive layer containing the compound which generates fluorescence at the time of exposure. According to such an approach, fluorescence occurs in a photosensitive layer at the time of exposure, and photochemical reaction arises according to an operation of both this fluorescence and incident light. It generates within a photosensitive layer, and since wavelength is longer than incident light, such as ultraviolet rays of short wavelength, especially this fluorescence is excellent in the permeability and/or reactivity within a layer. Therefore, in a photosensitive layer, even if the permeability of incident light originates in the ring contained in a layer

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and is reduced, a photochemical reaction fully advances according to an operation of fluorescence, finally it is high resolution and the pattern excellent in dry etching resistance can be obtained.

[0074] It is the aromatic compound illustrated by said first and second approach, and the compound of structure with which the symmetric property of a molecule collapsed can be used for the compound which generates fluorescence at the time of the exposure included in said photosensitive layer, for example. Especially the compound that contains in structure the ring which has the double bond which 4-12 which are used by the second approach conjugated may generate fluorescence very strongly at the time of exposure. In addition, it may be considered that the compound and aromatic compound which generate the fluorescence included in a photosensitive layer in this case are the same compound.

[0075] In addition, as a compound which generates fluorescence, various fluorescence coloring matter can also be used at the time of exposure. Moreover, various fluorescence coloring matter can be added to the aromatic compound mentioned above, and the effectiveness of fluorescence generating can also be raised to it. As an example of the fluorescence coloring matter concerned, an acridine orange, aminoacridine, Quinacrine, an anilinonaphthalene sulfonic acid derivative, ANSU roil yloxy stearin acid, Auramine O, chlorotetracycline; merocyanine, 1, cyanine system coloring matter like the 1 'dihexyl 2 and 2' OKISA carbocyanine; A dansyl sulfo amide, A dansyl choline, dansyl GARAKUSHIDO, dansyl tolidine, a dansyl chloride derivative like a dansyl chloride; Diphenyl hexa trien, Eosine, epsilon adenosine, an ethidium bromide, a fluorescein, former ISHIN, 4-benzoyl amide 4 'amino stilbenes 2 and 2' sulfonic acid, beta naphthyl triphosphoric acid, oxo-Norian coloring matter, a parinaric acid derivative, perylene, N-N phenylnaphthylamine, a pyrene, safranin O, fluorescamine, Fluoro SEIN isocyanate and 7-chloro 4 Nitrobenzo 2 OKISA 1 and 3 JIAZORU, A dansyl aziridine, 5-(iodoacetamide ethyl) aminonaphthalene 1 sulfonic acid, 5 iodoacetamide fluoro SEIN, N-(1 ANIRINO naphthyl 4) maleimide, N- (7 dimethyl 4 methyl bear nil maleimide and N-(3-pyrene) maleimide --) Eosine 5 An iodoacetamide, fluorescein Mercury acetate, 2-[4' (2 " iodoacetamide) aminonaphthalene, 6 sulfonic acid, eosine, a rhodamine derivative, etc. are mentioned. As for the loadings of these fluorescence coloring matter, it is desirable that it is at least 1 % of the weight - 50 % of the weight in photosensitive constituent (resist) solid content. There is a possibility that the loadings of fluorescence coloring matter may check conversely the definition and sensibility which there is no effectiveness, such as a sensibility rise, that it is the following about 1 % of the weight, and exceed 50 % of the weight.

[0076] By said third approach, since the compound which generates fluorescence is used for a photosensitive layer and the photochemical reaction in a photosensitive layer is promoted, the exposure line of all wavelength is employable. As the example, ultraviolet rays, far ultraviolet rays, vacuum ultraviolet radiation, synchrotron orbital RADIATION light, an electron ray, an X-ray, a gamma ray, an ion beam, etc. are mentioned.

[0077] Next, the fourth pattern formation approach of this invention is explained. The process which carries out the laminating of the photosensitive layer to which the fourth approach of this invention contains an aromatic compound on a substrate, and the fluorescence generating layer containing the compound which generates fluorescence at the time of fluorescence, The process which pattern exposure of said photosensitive layer and the fluorescence generating layer is carried out [ process ], generates fluorescence in this fluorescence generating layer, and produces photochemical reaction according to an operation of incident light and fluorescence in this photosensitive layer, The development of the photosensitive layer and fluorescence generating layer after exposure is carried out, and the process which makes the exposure section of this photosensitive layer remove or remain alternatively is provided.

[0078] The fourth approach of this invention applies said third approach. It is characteristic at the point which is mixed with a suitable resinous principle and forms in detail the compound which generates fluorescence as another layer, i.e., a fluorescence generating layer, at the time of the exposure contained

in the photosensitive layer in the third approach. According to the approach concerned, in a photosensitive layer, a photochemical reaction fully advances according to an operation of both the fluorescence produced in a fluorescence generating layer at the time of exposure, and incident light, finally it is high resolution and the pattern excellent in dry etching resistance can be obtained.

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[0079] In said fourth approach, the fluorescence agent of for example, an inorganic system can be used for the compound which constitutes a fluorescence generating layer. The salts currently generally used to fluorescent paint, a fluorescent lamp, the fluorescent substance for CRT, a pigment, etc. as an example of such a fluorescence agent are mentioned. As an example, it is  $\text{MgWO}_4$ ,  $\text{CaWO}_4$ , and 2 (PO<sub>4</sub> (calcium, Zn)). :  $\text{Ti}^+$ , Ba two P<sub>2</sub>O<sub>7</sub> : Ti and BaSi 2O<sub>5</sub> :P b<sup>2+</sup>, Sr two P<sub>2</sub>O<sub>7</sub> : Sn<sup>2+</sup>, SrFB 2O<sub>3.5</sub> : Inorganic-acid salts, such as  $\text{Eu}^{2+}$ ,  $\text{MgAl}_2\text{SiO}_5$ : $\text{Eu}^{2+}$ , and a tungstate, are mentioned.

[0080] Generally, since solubility is inadequate, it can be made the shape of detailed powder, and can distribute to a suitable solvent with a giant-molecule binder, and the fluorescence agent of these inorganic systems can form a layer by applying this mixed stock. Although what is necessary is just the polymeric materials which the above-mentioned fluorescence agent tends to distribute as a binder, if it takes multilayering with a photosensitive layer into consideration, a water soluble polymer is desirable. As an example of such polymeric materials, the copolymer of polyvinyl alcohol, a maleic acid, an acrylic acid, and a vinyl and an acrylic compound is mentioned. Moreover, although a fluorescence agent and a giant-molecule binder may distribute or dissolve in a solvent, a surfactant and a dispersant can also be blended if needed.

[0081] The range of the thickness of said fluorescence generating layer is about 0.05-0.5 micrometers preferably. When it deviates from this range, there is a possibility that the sensibility or definition of a photosensitive layer may fall remarkably.

[0082] Said fluorescence generating layer may be formed as the upper layer of a photosensitive layer, or lower layer any. When forming as the upper layer of a photosensitive layer, the mixed stock containing the compound which generates said fluorescence is applied by the thickness mentioned above on the photosensitive layer first formed like said first thru/or third approach. Then, it bakes at the temperature of about 70-120 degrees C, the solvent in mixed stock is distributed, and a fluorescence generating layer is obtained. Then, after it heat-treats exposure and if needed like said third approach and a suitable solvent or a suitable developer removes said fluorescence generating layer, the development of the exposed photosensitive layer is carried out, and a pattern is obtained.

[0083] On the other hand, in the case where said fluorescence generating layer is formed as a lower layer of a photosensitive layer, a fluorescence generating layer is first formed like the above on a substrate. Then, heat treatment and a development are performed like said third approach formation of a photosensitive layer, exposure, and if needed on this layer, and a pattern is obtained. In this case, said fluorescence generating layer can be flushed with a binder polymer with a spray method, or can exfoliate by the dry etching method. Although the latter approach is suitable especially, it is  $\text{CF}_4$  as etching gas in this case.  $\text{HBr}$  can be used.

[0084] Thus, in the case where a fluorescence generating layer is formed as a lower layer of a photosensitive layer, the photochemical reaction in the lower field, at which incident light cannot arrive easily in a photosensitive layer can be promoted more.

[0085]

[Example]

(Example 1) In the examples 1-2 of the following composition, the resinous principle blended with a photosensitive constituent was compounded.

Synthetic example 12 0.3 mols of naphthyl methacrylate, tert - 0.7 mols of butyl methacrylate were mixed with toluene 200g, and azo isobutyl nitril (azobisisobutyronitrile) 2g was added further.

Acetone after heating this mixed stock at the temperature of 70 degrees C for 8 hours It is dropped into - methanol solvent, and refines, and they are naphthyl methacrylate and tert. - The copolymer (resin A) with a butyl meta-chestnut rhe was obtained.

[0086] Moreover, the naphthyl methacrylate in the above-mentioned process was changed into vinyl naphthalene, a vinyl anthracene, and vinylcarbazole, and the copolymer (resin D-F) with the tert-butyl methacrylate of the copolymerization presentation 3:7 was obtained, respectively.

[0087] In addition, the beta naphthol novolak (resin C) of a commercial item was prepared. Each resin presentation is as follows.

Synthetic example 21 hydroxy 2 naphthyl aldehyde is mixed to a sodium ethoxide, and ethanol is

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removed. 1 hydroxy The sodium salt of 2 naphthyl aldehyde was obtained. then, a benzoyl chloride is dropped -- 1 benzoyloxy The 2-naphthol aldehyde was obtained. 1 benzoyloxy Add 0.9 mols of malonic acids to 0.25 mols of 2-naphthol aldehydes, add pyridine 10cc further, and it is made to react at the temperature of 110 degrees C for 2 hours, and is 1 benzoyloxy. 2 (beta carboxy) vinyl naphthalene was obtained. this -- 1 benzoyloxy 2 (beta carboxy vinyl naphthalene) 0.14 mol is dissolved in a 100 cc quinoline, 5g of copper powder is added, and it is made to react at the temperature of 220 degrees C further for 1 hour -- 1 benzoyloxy 2 vinyl naphthalene was obtained. Subsequently, 1 Benzoyloxy The polymerization of the 0.1 mols of the 2 vinyl naphthalene was carried out using azobisisobutironitoriru into benzene like the synthetic example 1, and Pori (1 benzoyloxy naphthalene) was obtained. An equivalent for the 0.5 mol (1 benzoyloxy vinyl naphthalene) monomer of this Pori was dissolved in the acetone, 1g of 1 moreN sodium-hydroxide water solutions was added and heated, and Pori (vinyl naphthol) (resin B) was obtained. The obtained polymer was reprecipitated with the acetone and the water-oxalic acid solution, and was refined.

[0088] The presentation of each resin is as follows.

Resin A -- Naphthyl methacrylate and tert - Copolymer with a butyl meta-chestnut rhe (molecular weight 20000, copolymerization presentation 3:7)

Resin B -- Pori (vinyl naphthol) (molecular weight 7000)

Resin C -- Beta naphthol novolak (commercial item: molecular weight 4500)

Resin D -- Vinyl naphthalene and tert - Copolymer with butyl acrylate (molecular weight 6000, copolymerization presentation 3:7)

Resin E -- A vinyl anthracene and tert - Copolymer with butyl acrylate (molecular weight 5500, a copolymerization presentation: 3:7)

Resin F -- Vinylcarbazole and tert - Copolymer with butyl acrylate (molecular weight 7000, copolymerization presentation 3:7)

In addition, following resin G-I was prepared. In addition, these resin does not contain a ring in structure.

[0089] Resin G -- Pori tert-butyl acrylate (molecular weight 12500)

Resin H -- Poly allyl compound methacrylate (molecular weight 24000)

Resin I -- Polyglycidylmethacrylate (molecular weight 20000)

Moreover, in the examples 3 and 4 of the following composition, the compound (dissolution retardant) which has association which may be decomposed with the acid blended with a photosensitive constituent was compounded.

Sodium hydride was made to react to the synthetic example 3 polyvinyl naphthol B, and some hydroxyl groups of a polyvinyl naphthol were used as sodium salt. Then, G tert-butyl 2 carbonate is made to react and it is tert. - The butoxycarbonyl radical was introduced and the compound (a) which has association which may be decomposed with an acid was obtained. tert in this compound - The rate of installation of a butoxycarbonyl radical was 20-mol % to all the hydroxyl groups of a polyvinyl naphthol.

It is bromoacetic acid tert, using potassium carbonate and potassium iodide as a catalyst at a synthetic example 4 polyvinyl naphthol. - Butyl ester is made to react and it is an acetic acid. tert-butyl was introduced and the compound (b) which has association which may be decomposed with an acid was obtained. Acetic acid in this compound The rate of installation of tert-butyl was 19-mol % to all the hydroxyl groups of a polyvinyl naphthol.

[0090] In addition, the compound which has association which may be decomposed with the following acid was prepared.

Compound c--tert - Butoxycarbonyl naphthol compound d -- Acetic acid tert-butyl-ized naphthol

compound e -- Tori (tert- butoxycarbonyl) anthra ROBIN compound f--tert - According to

buthoxycarbonyloxy phenanthrene and also the example 5 of the following composition, the photo-oxide generating agent blended with a photosensitive constituent was compounded.

After dissolving 0.2 mol of synthetic example 5 anthra ROBIN in the tetrahydrofuran and adding the methane sulfonyl chloride of molar quantity 3 times, 0.6 mols of triethylamines were dropped at \*\*\*\*. Then, after removing triethylamine and a tetrahydrofuran, it was made to recrystallize and anthra

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ROBINTORI (methane sulfonate) (compound g) was obtained.

[0091] In addition, the following photo-oxide generating agent (compound h-j) was prepared.

Compound h -- Naphthol naphthoquinonediazide Four sulfonate compounds i -- Triphenylsulfonium triflate compound j -- The methylsulfonyl acetonitrile and the photoinitiator cross linking reagent (compound k) shown below were prepared.

Compound k -- Melamine resin (Cymel 325)

A compound (component) in which the photosensitive constituent (resist) carried out preparation \*\*\*\* was blended according to the formula shown in Table 1, and the photosensitive constituents 1-17 were prepared. That is, after adding the acetic-acid ethylcellosolve of weight to the solid content of the component which the above-mentioned rate of a compounding ratio becomes the 3 times and agitating at a room temperature for 6 hours, it filtered through the Teflon filter of 0.2 micrometers of pore size, and the solution (varnish) of a photosensitive constituent was prepared.

[0092]

[Table 1]

表1 感光性組成物（レジスト）の処方

組成物 No.	樹脂成分 (重量%)	酸により分解し得る 結合を有する化合物 (重量%)	光酸発生剤 又は光架橋剤 (重量%)
1	A (97)	—	i (3)
2	A (95)	—	j (5)
3	B (67), G (30)	—	i (3)
4	G (50)	a (45)	g (5)
5	G (50)	b (45)	h (5)
6	C (47), G (50)	—	i (3)
7	D (97)	—	i (3)
8	E (97)	—	i (3)
9	F (97)	—	i (3)
10	G (70)	c (25)	g (5)
11	G (70)	d (30)	i (3)
12	G (65)	e (30)	g (5)
13	G (65)	f (30)	g (5)
14	B (80)	—	i (3), k (17)
15	H (47), B (50)	—	i (3)
16	I (47), B (50)	—	i (3)
17	B (70), G (20)	—	h (10)

[0093] Pattern formation was performed using the above photosensitive constituent. The spin coat of the photosensitive constituents 1-17 (solution) shown in Table 1 was carried out on the 5 inches silicon wafer, respectively, they were prebaked for 5 minutes on the 110-degree C hot plate, and the photosensitive layer (resist film) with a thickness of 0.9 micrometers was formed.

[0094] Subsequently, after carrying out pattern exposure (contact exposure) of the ArF excimer laser light (wavelength of 193nm) to said photosensitive layer, it baked for 2 minutes on the 110-degree C hot plate. Then, it was immersed in the developer which shows a wafer in Table 2 for 60 - 200 seconds, and said photosensitive layer was developed. Furthermore, the pattern which consists of predetermined

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Rhine and a tooth space was obtained by rinsing and drying.

[0095] In addition, the example concerned is equivalent to the first of this invention, and the second approach. The obtained pattern was observed with the scanning electron microscope (it abbreviates to SEM hereafter), and definition was evaluated. The result of the sensibility of the photosensitive layer (photosensitive constituent) in each pattern formation and definition (line breadth of a pattern) is written together to the following table 2.

[0096]

[Table 2]

表2 パターン形成（実施例1）

組成物 No	感 度 (mJ/cm <sup>2</sup> )	解 像 性 ( $\mu$ m)	現 像 液
1	120	0.4 (ポジ)	2.38% TMAH
2	200	0.4 (ポジ)	同 上
3	95	0.4 (ポジ)	同 上
4	115	0.4 (ポジ)	同 上
5	140	0.4 (ポジ)	同 上
6	240	0.4 (ポジ)	同 上
7	180	0.4 (ポジ)	同 上
8	210	0.4 (ポジ)	同 上
9	220	0.5 (ポジ)	同 上
10	120	0.4 (ポジ)	同 上
11	140	0.4 (ポジ)	同 上
12	160	0.5 (ポジ)	同 上
13	160	0.5 (ポジ)	同 上
14	75	0.5 (ネガ)	同 上
15	80	0.5 (ネガ)	エチル 2.38% TMAH
16	90	0.5 (ネガ)	同 上
17	150	0.5 (ポジ)	2.38% TMAH

・条件：コンタクト露光（ArFエキシマレーザ光）

ポストエクスポージャーバイク 110℃ 2分

・感光性層の膜厚：0.9  $\mu$ m

・現像液：TMAH（テトラメチルアンモニウムヒドロキシド）水溶液  
又はTMAHエタノール溶液

[0097] Moreover, Resin B was changed into Pori (vinyl phenol) (molecular weight 6000) among the resinous principles in the photosensitive constituent 3, and the photosensitive constituent 26 for a comparison was prepared. Enough patterns were not able to be obtained even if it carried out 500mJ exposure, when the pattern formation by ArF excimer laser exposure was tried according to the same approach and same conditions as an example 1 using this photosensitive constituent 26.

[0098] Furthermore in an example 1, the pattern obtained using the photosensitive constituent 3 is used as an etching-proof mask, and it is CF4. The etch rate was 47mm/min. when the plasma performed reactive ion etching.

[0099] Moreover, the etch rate was 140mm/min., when the pattern was formed on the substrate as a

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comparison according to the approach and conditions of an example 1 using the resist which consists of polymethylmethacrylate (PMMA) and rear KUTIGU ion etching was performed like the above by using this pattern as an etching-proof mask.

[0100] Compared with the pattern which adopted ArF excimer laser exposure and was obtained using PMMA, it is clearer than such a result the pattern's obtained according to the example of this invention to have about 3 about times many dry etching [ as this ] resistance.

(Example 2) The resinous product blended with a photosensitive constituent was compounded and prepared as follows.

[0101] The commercial acetal resin S lek BLS (Sekisui Chemical Co., Ltd. make) (rate % of 70 mols of acetalization) (resin J) was prepared as acetal resin blended with a photosensitive constituent.

[0102] Moreover, in the synthetic examples 6 and 7, another acetal resin K and L blended with a photosensitive constituent was compounded.

3ml of glyoxylic acids and 4.5ml of concentrated sulfuric acid were dissolved in 30ml of water at synthetic example 6 poly vinyl alcohol 2g (molecular weight 22500), and it reacted at 60 degrees C for 48 hours. It neutralized by the sodium hydroxide after a reaction, the re-degree was carried out with the water-methanol, and the glyoxylic-acid ghost (resin K) of polyvinyl alcohol was obtained. (The rate of acetalization is 20-mol %)

According to synthetic example 7 reference (Colloid Polym Sci.252 and 294 (1974)), amino acetalization polyvinyl alcohol (resin L) was compounded from polyvinyl alcohol (molecular weight 22500). (The rate of amino acetalization is 6%)

The epoxy resin blended with a photosensitive constituent in the synthetic examples 8 and 9 as an epoxy resin blended with a photosensitive constituent was compounded.

0.1-mol epichlorohydrin was added to the synthetic example 81 and 0.05 mols of 5 naphthalene diols, 0.25g of water and 80 degrees C of NaOH4.0g were added to this, unreacted epichlorohydrin was removed by 30mmHg after the 2-hour reaction, and the epoxy resin was extracted with toluene. Reduced pressure distilling off of the toluene was carried out, and the epoxy resin (resin M) which introduced 1 and 5 naphthalene diol was obtained.

the synthetic example 94 and 4" -- one-mol epichlorohydrin was added to 0.05 mols (dihydroxy naphthalene) of methylenebises, 0.25g of water and 80 degrees C of NaOH0.8g were added to this, after the 2-hour reaction, by 30mmHg, unreacted epichlorohydrin was removed, it came out, and the ether extracted epoxy. Reduced pressure distilling off of the ether was carried out, and the rate 4 of low installation and the epoxy resin (resin N) which introduced 4" methylenebis (dihydroxy naphthalene) were obtained.

[0103] Moreover, 1 of marketing, the epoxy resin (Dainippon Ink make) (resin P) which introduced 6 naphthalene diol, 4 of marketing, the epoxy resin (Dainippon Ink make) (resin Q) which introduced 4" methylenebis (dihydroxy naphthalene), and alicyclic diepoxy CY179 (Ciba-Geigy make) (resin S) were prepared.

[0104] Moreover, as a photo-oxide generating agent, the nitrobenzyl cyclohexyl carbamate (the Midori chemistry company make) (compound n) was prepared as triphenylsulfonium triflate (the Midori chemistry company make) (compound l), 2-(4'- methoxy naphthyl)-4, 6-screw (TORIKURORO methyl - 1, 3, 5 - triazine) (the Midori chemistry company make) (compound m), and an optical alkali generating agent.

[0105] A compound which was mentioned above was blended according to the formula shown in Table 3, and the photosensitive constituents 18-23 were obtained. That is, after adding the cyclohexanone or water of weight to the solid content of the rate of a compounding ratio shown in Table 3 the 3 times and agitating at a room temperature for 6 hours, it filtered through the Teflon filter of 0.2 micrometers of pore size, and the solution of a photosensitive constituent was prepared.

[0106]

[Table 3]

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表 3

組成物 No.	アセタール 樹脂成分 (重量%)	エポキシ 樹脂成分 (重量%)	光酸又は アルカリ発生剤 (重量%)
18	J (73)	M (25)	l (2)
19	K (74)	N (25)	l (1)
20	K (75)	N (20)	m (5)
21	K (75)	N (20)	n (5)
22	L (78)	P (20)	l (2)
23	K (49)	S (20), Q (20)	l (2)

[0107] The spin coat of the photosensitive constituent (solution) shown in Table 1 was carried out on the 5 inches silicon wafer, respectively, it was prebaked for 5 minutes on the 110-degree C hot plate, and the photosensitive layer (resist film) with a thickness of 0.9 micrometers was formed.

[0108] Subsequently, after carrying out pattern exposure (contact exposure) to said photosensitive layer with an ArF excimer laser, it baked for 2 minutes on the 110-degree C hot plate. Then, it was immersed in the developer which shows a wafer in Table 4 for 60 - 200 seconds, and said photosensitive layer was developed. Furthermore, the pattern which consists of predetermined Rhine and a tooth space was obtained by rinsing and drying.

[0109] In addition, the example concerned is equivalent to the first of this invention, and the second approach. The obtained pattern was observed with the scanning electron microscope (it abbreviates to SEM hereafter), and definition was evaluated. The result of the sensibility of the photosensitive layer (photosensitive constituent) in each pattern formation and definition (line breadth of a pattern) is written together to the following table 4.

[0110]

[Table 4]

表 4

組成物 No.	感度 (mJ/cm <sup>2</sup> )	解像性 ( $\mu$ m)	現像液
18	15	0.5 $\mu$ m	MIBK
19	25	0.5 $\mu$ m	3.0%TMAH
20	80	0.5 $\mu$ m	3.0%TMAH
21	75	1.0 $\mu$ m	3.0%TMAH
22	20	0.5 $\mu$ m	MIBK
23	10	0.5 $\mu$ m	MIBK

・条件：コンタクト露光 (ArFエキシマレーザ光)

ポストエクスポージャーベイク 110℃ 2分

・感光性層の膜厚：0.9  $\mu$ m

・現像液：MIBK (メチルイソブチルケトン)

又はTMAH (テトラメチルアンモニウムヒドロキシド) 水溶液

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[0111] Moreover, the absorbance of 1-micrometer thickness in 193nm of the pattern of the photosensitive constituents 18-23 was measured. The result is shown in Table 5. On the other hand, the absorbance was measured as an example 1 of a comparison about photoresist OFPR-800 (Tokyo adaptation make) of marketing as well as the photosensitive constituents 18-23. The result is shown in Table 5.

[0112] In an example 2, the pattern obtained using the photosensitive constituents 18-23 and photoresist OFPR-800 is used as an etching-proof mask, and it is CF4. The etch rate in the reactive-ion-etching (50m torr, 80W) case was measured by the plasma. The result is written together to Table 5.

[0113]

[Table 5]

表 5

感光性組成物番号	吸光度	エッチング速度 (nm/min)
18	0.6	3.1
19	0.5	3.0
20	0.5	3.5
21	0.7	3.0
22	0.6	3.2
23	0.5	3.5
比較例	30.0	3.0

[0114] Like the above, it turns out that the resist of this example excels [ absorbance / in 193nm ] in dry etching resistance small.

(Example 3)

The resinous principle blended with a photosensitive constituent was compounded.

0.7-mol glycidyl methacrylate was mixed for the trimethylsilyl methacrylate of 100.3 mols of synthetic examples in 200g of toluene, and 2g (azobisisobutyronitrile) of azo isobutyl nitril was added, and it heated at 70 degrees C for 8 hours, and carried out under \*\* into the acetone-methanol solvent, and 3:7 copolymers of trimethylsilyl methacrylate and glycidyl methacrylate were obtained. (Molecular weight 10000) After agitating this for 1 hour and detrimethylsilylating it by the acetone-acetic-acid-water mixed solvent system, with water, the re-degree was carried out, it dried, and methacrylic-acid-guru SHIJIRU methacrylate 3:7 copolymer was obtained. ((Q) Resin)

Moreover, as another resinous principle blended with a photosensitive constituent, 1 and 5 dihydroxy naphthalene (Aldrich make) (resin R) were prepared.

[0115] The above-mentioned compound was blended according to the formula shown in Table 6, and the photosensitive constituent 24 was obtained. That is, after adding the cyclohexanone or water of weight to the solid content of the rate of a compounding ratio shown in Table 6 the 3 times and agitating at a room temperature for 6 hours, it filtered through the Teflon filter of 0.2 micrometers of pore size, and the solution of a photosensitive constituent was prepared.

[0116]

[Table 6]

表 6

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組成物 No	樹脂成分 (重量%)	樹脂成分 (重量%)	光酸発生剤
24	O (74)	R (25)	1 (1)

[0117] The spin coat of the photosensitive constituent 24 (solution) shown in Table 6 was carried out on the 5 inches silicon wafer, respectively, it prebaked for 5 minutes on the 110-degree C hot plate, and the photosensitive layer (resist film) with a thickness of 0.9 micrometers was formed.

[0118] Subsequently, after carrying out pattern exposure (contact exposure) to said photosensitive layer in the source of exposure shown in Table 7, it baked for 2 minutes on the 110-degree C hot plate. Then, it was immersed in the developer which shows a wafer in Table 7 for 60 - 200 seconds, and said photosensitive layer was developed. Furthermore, the pattern which consists of predetermined Rhine and a tooth space was obtained by rinsing and drying.

[0119] In addition, the example concerned is equivalent to the first of this invention, and the second approach. The obtained pattern was observed with the scanning electron microscope (it abbreviates to SEM hereafter), and definition was evaluated. The result of the sensibility of the photosensitive layer (photosensitive constituent) in each pattern formation and definition (line breadth of a pattern) is written together to the following table 7.

[0120]

[Table 7]

表 7

組成物 No	感 度 (mJ/cm <sup>2</sup> )	解 像 性 ( $\mu$ m)	現 像 液
24	30	0.5 $\mu$ m	3.0%TMAH

- ・条件：コンタクト露光（ArFエキシマレーザ光）  
ポストエクスポージャーベイク 110℃ 2分
- ・感光性層の膜厚：0.9  $\mu$ m
- ・現像液：TMAH（テトラメチルアンモニウムヒドロキシド）水溶液

[0121] Moreover, the absorbance of 1-micrometer thickness in 193nm of the pattern of the photosensitive constituent 24 was measured. The result is shown in Table 8. The absorbance which, on the other hand, measured photoresist OFPR-800 (Tokyo adaptation make) of marketing similarly as an example of a comparison is also shown in Table 8.

[0122] In an example 3, the pattern obtained using the photosensitive constituent 24 and photoresist OFPR-800 is used as an etching-proof mask, and it is CF4. The etch rate in the reactive-ion-etching (50m torr, 80W) case was measured by the plasma. The result is written together to Table 8.

[0123]

[Table 8]

表 8

感光性組成物番号	吸 光 度	エッチング速度 (nm/min)
24	0.5	3.0
比 較 例	30.0	3.0

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[0124] It turns out like the above that the resist of this example excels [ absorbance ] in dry etching resistance small.

(Example 4) The pyrene (compound which generates fluorescence) equivalent to 3% of the weight of the solid content of opposite *Perilla frutescens* (L.) Britton var. *crispa* (Thunb.) Decne. was added to the photosensitive constituent 17 (solution), optical filtering was performed again, and it considered as the photosensitive constituent 25. According to the same approach and same conditions as an example 1, the pattern was formed using this constituent. As a developer, 2.38% of TMAH water solution was used.

[0125] In addition, the example concerned is equivalent to the third approach of this invention. The sensibility of the photosensitive layer in an example 4, definition, and the acquired cross-section

configuration of a pattern are shown in the following table 3. Moreover, in Table 3, sensibility, definition (line breadth of a pattern), and the cross-section configuration of a pattern are written together about the case where pattern formation is performed using the photosensitive constituent 17 in an example 1.




(Example 5)  $\text{MgWO}_4$  5 % of the weight (compound which generates fluorescence) of powder, and polyacrylic acid were mixed underwater, and surfactant Epicoat 1% was added further. The obtained dispersion liquid were applied on the substrate, it heated for 5 minutes at the temperature of 200 degrees C, and the thin film of 0.1 micrometers of thickness, i.e., a fluorescence generating layer, was formed. this thin film top -- the photosensitive constituent 17 (solution) -- a spin coat -- carrying out -- the same approach and same conditions as an example 1 -- exposure -- and the development was carried out and the pattern was formed. As a developer, 2.38% of TMAH water solution was used.

[0126] In addition, the example concerned is equivalent to the fourth approach of this invention. The sensibility of the photosensitive layer in the example concerned, definition (line breadth of a pattern), and the cross-section configuration of a pattern are shown in the following table 9.

[0127]

[Table 9]

表9 パターン形成 (試験例 1. 2. 3)

試験例	感 度 ( $\text{mJ}/\text{cm}^2$ )	解 像 性 ( $\mu\text{m}$ )	パターン断面形状
※ 1	1 5 0	0. 5	
※ 2	1 2 0	0. 4	
※ 3	1 2 0	0. 4	

[0128] \* Example 1 of a trial -- The pattern was formed using the photosensitive constituent 17.

Example 2 of a trial -- The pattern was formed using the photosensitive constituent 25 (constituent which added the compound which generates fluorescence).

[0129] Example 3 of a trial -- The fluorescence generating layer was formed on the substrate and the pattern was formed using the photosensitive constituent 17 on this layer.

(Example 6) The photosensitive layer which consists of a photosensitive constituent 17 was formed on the substrate. On this layer, the dispersion liquid of the compound which generates the fluorescence used in the example 3 were applied, it heated for 5 minutes at the temperature of 200 degrees C, and the thin film of 0.1 micrometers of thickness, i.e., a fluorescence generating layer, was formed. Then, on the photosensitive layer and the thin film, after exposing the electron ray of 20keV, the development was carried out on the same approach and same conditions as an example 1, and the pattern was formed.

[0130] At the example concerned, it is sensibility  $\text{C}/\text{cm}^2$  of 5micro. The pattern with a line breadth of 0.3 micrometers was obtained. In addition, in the case where did not form a fluorescence generating layer on the substrate, but a direct photosensitivity layer is formed as a comparison, a pattern was not able to be obtained at all.

[0131]

[Effect of the Invention] As explained in full detail above, according to this invention, the approach which is stabilized and can form the pattern which is the pattern formation approach which adopted exposure of short wavelength, and is high resolution, and was excellent in dry etching resistance can be offered. The approach of this invention can be effectively applied to the photolithography in manufacture processes, such as a semiconductor device, and the industrial value is very large.

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[Translation done.]

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CORRECTION OR AMENDMENT

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[Claim 1] the process which forms the photosensitive layer containing an aromatic compound on a substrate, and a long wave [ in / to said photosensitive layer / the absorption spectrum of said aromatic compound ] -- the process which it is [ process ] shorter than the maximum wave length of the 3rd absorption band from a merit side, and pattern exposure of the light of long wave length is carried out [ process ] from the maximum wave length of the 4th absorption band, and produces photochemical

reaction in this photosensitive layer,

The pattern formation approach of providing the process which carries out the development of the photosensitive layer after exposure.

[Claim 2] The pattern formation approach according to claim 1 that said exposure wavelength is characterized by said aromatic compound being 170nm or more 150nm or less, including a benzene ring frame.

[Claim 3] The pattern formation approach according to claim 1 that exposure wavelength is characterized by said aromatic compound being 230nm or more 190nm or less, including an anthracene ring frame.

[Claim 4] The process which forms the photosensitive layer containing the aromatic compound which contains the ring which has 12 or less or more 4 conjugated double bond in structure on a substrate, The process which pattern exposure of the with a 180nm or more wavelength [ 220nm or less ] ultraviolet rays is carried out [ process ], and makes said photosensitive layer produce photochemical reaction in this photosensitive layer,

The pattern formation approach of providing the process which carries out the development of the photosensitive layer after exposure.

[Claim 5] The pattern formation approach according to claim 4 characterized by said ring which has 12 or less or more 4 conjugated double bond being a compound ring which six membered-rings combined.

[Claim 6] Said ring which has 12 or less or more 4 conjugated double bond is the pattern formation approach according to claim 5 characterized by being chosen from naphthalene, an anthracene, and a phenanthrene.

[Claim 7] Said photosensitive layer is the pattern formation approach according to claim 4 characterized by including the copolymer which contains naphthyl methacrylate as a monomer.

[Claim 8] Said photosensitive layer is the pattern formation approach according to claim 4 characterized by including the copolymer which contains vinyl naphthalene as a monomer.

[Claim 9] The ring which has said 12 or less or more 4 conjugated double bond is the pattern formation approach claim 4 characterized by being less than [ more than 75% % of the weight 100 % of the weight ] among all the rings in a photosensitive layer thru/or given in 8 terms.

[Claim 10] Said photosensitive layer is the pattern formation approach given in claim 4 term characterized by containing the compound which generates an acid or alkali by the exposure of the polymer containing the vinyl compound which has an epoxy group in a side chain, the polymer containing the vinyl compound which has a naphthalene ring in a side chain, the polyhydroxy compound that contains a naphthalene ring in a frame and light, or ionizing radiation.

[Claim 11] Said ring which has said 12 or less or more 4 conjugated double bond is the pattern formation approach according to claim 4 characterized by having the substituent of protective group OR' (R' is tert-butyl or a tert-butoxycarbonyl radical) of a hydroxyl group or a hydroxyl group.

[Claim 12] With a 180nm or more wavelength [ said / 220nm or less ] ultraviolet rays are the pattern formation approaches claim 4 characterized by being the light which made the light source the 5 time tidal-wave length of an ArF excimer laser or an YAG laser thru/or given in 11 terms.

[Claim 13] The process which forms on a substrate the photosensitive layer which generates fluorescence including an aromatic compound at the time of exposure, The process which pattern exposure of said photosensitive layer is carried out [ process ], generates fluorescence, and produces photochemical reaction according to an operation of incident light and fluorescence in this photosensitive layer,

The pattern formation approach of providing the process which carries out the development of the photosensitive layer after exposure.

[Claim 14] Said photosensitive layer is the pattern formation approach according to claim 13 characterized by containing the compound which generates fluorescence at the time of an aromatic compound and exposure.

[Claim 15] The compound which generates said fluorescence is the pattern formation approach according to claim 14 characterized by being a fluorochrome.

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[Claim 16] Said photosensitive layer is the pattern formation approach according to claim 13 characterized by containing the aromatic compound which generates fluorescence at the time of exposure.

[Claim 17] The process to which the laminating of the photosensitive layer which contains an aromatic compound on a substrate, and the fluorescence generating layer containing the compound which generates fluorescence at the time of exposure is carried out,

The process which pattern exposure of said photosensitive layer and the fluorescence generating layer is carried out [ process ], generates fluorescence in this fluorescence generating layer, and produces photochemical reaction according to an operation of incident light and fluorescence in this photosensitive layer,

The pattern formation approach of providing the process which carries out the development of the photosensitive layer and fluorescence generating layer after exposure.

[Claim 18] Said fluorescence generating layer is the pattern formation approach according to claim 17 characterized by containing the compound containing the ring which has 12 or less or more 4 conjugated double bond which generates fluorescence.

[Claim 19] The ring which has said 12 or less or more 4 conjugated double bond is the pattern formation approach according to claim 18 characterized by being a compound ring compound.

[Claim 20] The compound which generates said fluorescence is the pattern formation approach according to claim 17 characterized by being a fluorochrome.

[Claim 21] The compound which generates said fluorescence is the pattern formation approach according to claim 17 characterized by being the fluorescence agent of an inorganic system.

[Claim 22] Said fluorescence generating layer is the pattern formation approach according to claim 17 characterized by including a giant-molecule binder.